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OF THE

# Elisha Mitchell Scientific Society

ISSUED QUARTERLY

CHAPEL HILL, N. C., U. S. A.

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JOURNAL
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# NOTES ON THE PETROGRAPHY OF THE GRANITES OF CHAPEL HILL, NORTH CAROLINA[1]

BY H. N. EATON

Thd village of Chapel Hill, North Carolina, is located upon a gently rounded knob of granite rocks within the "Carolina Metamorphic Slate and Volcanic Belt," bounded upon the east by Triassic sandstone, and on the south and west by sedimentary and pyro-clastic rocks of unknown age. Northward the granite becomes rapidly more basic, reaching a quartz-mica-diorite, or grano-diorite. Rocks resembling true diorites macroscopically are adjacent on the north. Aplite dikes exist everywhere, and a suite of specimens can be easily collected showing a gradation from this binary type to rocks containing biotite and hornblende, The range in color and texture varies from fine grained, white, acid rocks, to those which are dark, medium, and coarse grained.

## PREVIOUS WORK

No previous attempt has been made to study the rocks microscopically. The only place in geological literature where reference has beed made to the area is in a recent publication of the North Carolina Geological Survey.[2] This is merely a brief description of the areal extent and field appearance of the more striking types of granite and diorite in the neighborhood.

1 Presented in outline before the North Carolina Academy of Science, Durham, N. C., May 1, 1909.

2 North Carolina Geological Survey, Bull. No. 2, "The Building and Ornamental Stones of North Carolina," by Watson, Laney, and Merrill, Raleigh, 1906, pp. 55-57.

While the present microscopic work was being done the writer[2] published a description of micropegmatite in one of the binary granites.

The following notes are based on the examination of thin sections only, no chemical analyses having beed made. The numbers refer to specimens in the Geological Laboratory of the University of North Carolida.

### No. 35. Binary Granite.

In handspecimen—fine grained, grayish white, much decomposed; showing only quartz and feldspar.

In thin section—contains quartz, orthoclase, plagioclase, and some epidote.

The crystals aye not all uniform in size, large and small being mixed promiscuously. Plagioclase and quartz occur in the most abundance, and the orthoclase in a relatively insignificant amount.

Maximum albite twinning striations perpendicular to M on the plagioclase gave +9 degrees, thus placing the mixture between oligoclase and andesine.

The orthoclase is in moderately large crystals.

Epidote occurs in several connected lines, probably filling veins.

### No 10-A. Muscovite Granite.

In handspecimen—a medium grained, pink rock, consisting essentially of pink feldspar and quartz.

In thin section—composed of quartz, orthoclase, microcline, plagioclase, muscovite. chlorite, and magnetite. It is mainly a feldspar rock with porphyritic crystals of plagioclase and alkali feldspar, surrounded by a rubble of small quartz and feldspar fragments.

The plagioclase is the most abundant mineral, belonging to the species oligoclase, and displaying albite twinning in very fine striations, also carlsbad twinning. The crystals are short and irregular in outline, and frequently exhibit slight bending as though caused by strain.

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2 This Journal, vol. 24, No. 3, Nov. 1908, pp. 104-105

Microcline is quite abundant; orthoclase, less so.

Graphic intergrowths between plagioclase and the alkali feldspars are common.

Quartz is confined to the fine crystals of the groundmass.

Muscovite occurs in fine shreds bent in long string-like masses, usually near grains of magnetite.

Chlorite was observed in a few small scales.

No. 10-B. Biotite Granite.

In handspecimen—a medium to fine grained, mottled rock showing on fresh fracture quartz, feldspar, a colored silicate, and a metallic looking mineral.

In thin section—contains quartz, orthoclase, plagioclase, biotite, magnetite, and titanite.

The magnetite is disseminated thickly through the slide in crystals of appreciable size. In one place a relatively large mass surrounds an equally large mass of titanite.

Titanite is quite abundant.

Biotite occurs in short crystals. It is mainly altered to chlorite, and is pleochroic, the range being from straw yellow to grass green.

Plagioclase is of rather sparing occurrence and is near oligoclase in composition, with maximum extinction angles of 7 and 8 degrees.

Orthoclase occurs in many forms. The crystals are of various sizes, frequently enclosing small particles of plagioclase.

The microcline grating structure can be observed in a number of instances but is indistinct.

Quartz is found well crystallized in large forms.

No. 18. Biotite Granite.

In handspecimen—a medium to fine grained rock, much decomposed, showing quartz, feldspar, and a dark silicate, probably biotite in an advanced stage of chloritization.

In thin section—contains essential quartz, feldspar and biotite; with accessory magnetite, titanite, and zircon. Epidote appears in a vein, and chlorite as a decomposition product.

Biotite is disseminated sparingly through the slide. It is the only dark colored silicate present, and is universally altered to chlorite.

Oligoclase is quite abundant. The albite twin striations are fine. Carlsbad twinning was noted.

Orthoclase and microcline are abundant, the latter somewhat less so of the two. All of the feldspars are much kaolinized.

Quartz occurs in the usual manner, ffilling in the interstices between the earlier formed minerals.

Magnetite occurs sparingly in a few small grains.

Titanite occurs in a few localities in large crystals.

Zircon was observed in one place.

No. 23. Biotite Granite.

In handspecimen—a medium grained, mottled, pink rock; showing quartz, pink feldspar, and green biotite.

In thin section—contains quartz, orthoclase, microcline, plagioclase, and biotite.

The biotite occurs in small crystals arranged in a number of large clusters. It is of the green variety.

Plagioclase is isolated in a number of small, stout prisms, much kaolinized. Many feldspar crystals, kaolinized beyond recognition, are probably plagioclase.

Orthoclase and microcline are very abundant in square and rectangular prisms.

Quartz occurs in well defined crystals of uniform size.

The uniformity in size of the quartz and feldspar forms is the feature of the slide.

No. 16. Biotite Granite.

In handspecimen—a coarse grained, mottled rock, with a peculiar blending of dark green and pink on weathered surfaces. There appears to be an abundance of quartz, feldspar (probably orthoclase), and a dark colored silicate arranged in clusters. This last is with difficulty resolved with the hand lens into fine flakes of biotite.

In thin section—composed of quartz, orthoclase, microcline,

Plagioclase, biotite, titanite, pyrite, and apatite.

The biotite is the only colored silicate, is green in color, and only sparingly present.

The plagioclase is oligoclase, and not abundant. It occurs in irregularly bounded crystals, much kaolinized.

Microcline is very abundant in relatively large crystals.

Orthoclase covers a total area about equal to the microcline.

Quartz occurs in large irregular masses.

Pyrite is found in several large grains. Incident light shows an individual mass to be composed of an unaltered core of pyrite surrounded by steely hematite, the whole in turn, encased in a rim of hematite.

Titanite occurs in a few scattered crystals.

Apatite occurs in small crystals near the biotite.

### No. 13. Biotite—hornblende granite.

In handspecimen—a coarse grained, mottled, pink rock, much weathered. with much pink feldspar, some quartz, and hornblende.

In thin section—contains magnetite, titanite, biotite. hornblende, plagioclase, and quartz.

Biotite occurs in light green and brown to deep green colors. The brown type is in the smallest crystals and is frequently chloritized. The green variety is found in larger crystals and is less common.

Hornblende occurs in comparatively large amount in large forms. Pleochroism, marked; yellow to deep grass green. Interference, high. Twinning observed.

The plagioclase crystals are large and much kaolinized. Twin striations, very fine. Species, oligoclase.

Orthoclase occurs in large masses, with indistinct boundaries in places.

A few large microcline crystals are present.

### No 8. Hornblende Granite.

In handspecimen medium to coarse grained, mottled rock; showing flesh colored feldspar, quartz, and much hornblende. The specimen is much weathered.

In thin section—composed of essential quartz, orthoclase, microcline, plagioclase, and hornblende; with biotite, magnetite, and apatite as accessories, and chlorite and kaolin as decomposition products.

Hornblende is abundant in irregular crystals and masses of crystal fragments, showing absorption by the later formed quartz and feldspar. Color, green. Strongly pleochroic, grass green to straw yellow. Interference colors, high greens and browns. Some crystals show twinning.

Biotite occurs sparingly. Color, grass green with marked pleochroism.

The plagioclase is oligoclase, occuring in stout idiomorphic crystals, often highly kaolinized.

Orthoclase occurs abundantly in large allotriomorphic crystals.

Microcline is quite abundant, its period of crystallization being between the orthoclase and quartz.

Quartz is very abundant.

Magnetite and apatite are found near the colored silicates.

Chlorite results from biotite decomposition.

No. 9. Quartz-mica Diorite.

In handspecimen—a medium grained, uniformly dark gray rock, showing an abundance of feldspar and hornblende, and some quartz.

In thin section—composed of quartz, plagioclase, biotite, hornblende, and magnetite.

The hornblende occurs in profusion in long crystals, commonly twinned. Pleochroic; light straw yellow to light green. Interference colors, high. The majority of the crystals are uniform in size, but many smaller ones occur in the groundmass.

Plagioclase, species oligoclase, comprises the larger part of the rock and the crystals are of various sizes, the largest almost amounting to phenocrysts. Smaller crystals are abundant in the groundmass. Albite and carlsbad twinning, universal. Zoning, common. All crystals are idiomorphic, and their boundaries are distinct.

Biotite of the greenish brown variety, is quite common.

Quartz fills in the interstices between the other minerals.

Magnetite is found in a few scattered grains.

The groundmass is composed of smaller crystals of quartz, feldspar, hornblende, and biotite.

University of North Carolina.

# CONDENSATION OF CHLORAL WITH PRIMARY AROMATIC AMINES. III[1]

A. S. WHEELER AND STROUD JORDAN

This research was undertaken, first, to establish the constitution of derivatives of chloral-di-phenamine compounds obtained by the action of bromine and, second, to extend the limited work already done on the condensation of chloral with primary aromatic amines, including a study of their behavior.

## HISTORICAL CONSIDERATIONS

The first real condensation product of an aromatic amine with chloral is tri-chlor-ethylidene-di-phenamine ($C_{14}H_{13}N_2Cl_3$), which is prepared by the action of chloral upon aniline, one molecule of chloral to two molecules of aniline. This reaction was carried out by Schiff and Amato[2] in the year 1875. O. Wallach also prepared this same compound in the same year,[3] independently of the first two workers and he also prepared the condensation products of xylidene and paratoluidine. Later on this reaction was extended to other unsubstituted aromatic amines by A. Eibner,[4] who succeeded in preparing the condensation products of aniline and para-toluidine. Still later, this reaction has been extended to some of the remaining unsubstituted aromatic amines by Wheeler and Jordan[4],[5] who succeeded in making the condensation product of chloral and ortho-toluidine. These reactions have been carried out in a very uniform manner, except for the solvent used, for each product was made by the reaction of one molecule of chloral upon two molecules of the unsubstituted aromatic amine,

[1] This paper forms part of a thesis presented to the Faculty of the University of North Carolina in May 1909 by Stroud Jordan, candidate for the degree of Doctor of Philosophy.

[2] Gazz. chim. ital. **I**: 376. 1871.

[3] Ber. d. Chem. Ges. **4**: 668. 1871.

[4] Ann. Chem. (Liebig) **302**: 340. 1898.

[5] Journal American Chemical Society, **30**: 141. 1908.

with or without the aid of a solvent. It has been possible to obtain a product which will be very pure, by the action of chloral hydrate with the free amine, as Alexander Eibner did, or by the action of chloral upon the amine, as A. Eibner did and as we have done, or still, by the action of chloral upon the unsubstituted primary aromatic amines in the presence of a solvent, as we have done in the majority of our reactions.

The first substituted primary aromatic amines were condensed with chloral by A. Eibner, when he succeeded in preparing tri-chlor-ethylidene-di-metachlor-phenamine,[1] tri-chlor-ethylidene-di-para-chlor-phenamine,[2] and tri-chlor-ethylidene-di-para-nitro-phenamine[3]. He also extended his study of this condensation reaction to the reaction of chloral and di-chlor-aniline, which he was able to get[1] and to the reaction of chloral and tri-chlor-aniline which he was not able to carry out. Following this work of A. Eibner we have the work of Wheeler and Weller[3], who succeeded in preparing the tri-chlor-ethylidene-di-ortho-phenamine, the work of Wheeler and Miller[3], upon para-brom-aniline and chloral obtaining thus tri--chlor-ethylidene-di-para-brom-phenamine; the work of Wheeler and Dickson[3] on para-anisidine and chloral, and Niementowski and Orzechowski's work[4] on chloral and anthranilic acid. These reactions were all carried out in the same proportions as were used in the unsubstituted primary aromatic amines, that is, two molecules of the substituted primary aromatic amine and one molecule of chloral with or without a solvent.

### NITROGÉN HALIDES

The most thorough study made of nitrogen halides has been made by Chattaway and Orton[5]. They succeeded in getting one hydrogen in the aniline side chain,($NH_2$), replaced by a halogen when the other hydrogen had been replaced by a negative group,

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[1] Ann. Chem. (Liebig), **302**: 340. 1898.
[2] Journal American Chemical Society, **24**: 1063. 1902.
[3] Journal American Chemical Society, **30**: 136. 1908.
[4] Ber. d. Chem. Ges., **28**: 2812. 1895.
[5] Journal London Chemical Society, **75**: 1046. 1899.

as CHO or $CH_3CO$. By this means they were able to prepare a number of nitrogen halides, all of which were unstable and tended to isomerize, the halogen going to the para position, if it was unoccupied, and when this position was filled going to the hydrogen ortho to the amino group.

### CONDENSATIONS DESCRIBED IN THIS THESIS

Thirteen new compounds are described in this thesis. They comprise the condensatisn products of chloral with the following primary amines: meta-amino-benzoic acid, para-amino-benzoic acid, 4-nitro-2-toluidine. 2-nitro-4-toluidine, 3-nitro-4-toluidine, meta-chlor-para-toluidine, 5-brom-2-amino-benzoic acid, 4-brom-2-nitraniline, 4-brom-3-nitraniline, para-iodo-aniline, 4-brom-I-napthylamine, and para-amino-aceto-phenone. The behaviour of tri-chlor-aniline and chloral was also studied, not only in high boiling point solvents but also in a sealed tube.

### THEORETICAL CONSIDERATIONS

It will be seen from the results of this work as well as that of previous workers, that chloral does not combine with all primary aromatic amines. It is to be observed further that the condensations are not made with uniform readiness, for Eibner found that when three negative groups are substituted in the benzene ring no condensation takes place and we find that when two negative groups are present, of unlike character, the reaction generally requires the addition of much heat in order that it may take place in the best possible manner. It is necessary to boil the mixture of chloral and the amine for at least one hour and fifteen minutes, in order that the reaction may be completed. We have also observed that when the two negative groups in the benzene ring are similar that the reaction proceeds easier than in the former case but still requires the addition of heat. In the case of one negative group, present in the benzene ring, reaction will take place very slowly and in a very moderate manner, when chloral is mixed with the amine in the presence of some good solvent. When no negative groups are present in the benzene ring, the reaction takes place immediately, with the liberation of a large amount of

heat, either in the presence of a solvent or without it. Generally speaking, the condensation products containing the most negative groups are the most stable, and those containing no negative groups the least stable. All these condensation products are broken down on brominating in the presence of glacial acetic acid, splitting off chloral and giving either a bromine derivative of the free amine or an acid salt of the free amine or both. Strong mineral acids will break all these condensation products down into the corresponding salt of the free amine, with the liberation of chloral. In the case of the strongly negative products, alkalies yield an hydroxy derivative. Such a compound is obtained most readily by the action of alcoholic potash. In the case of the condensation products containing no negative groups, in the benzene ring, strong alkalies break them down into the free amine and chloral, only with great difficulty and on prolonged heating, hence they are very stable towards alkalies.

The behaviour of all these condensation products with bromine seem to indicate a regular law for the position of the substituted bromine atom. When they are treated with bromine and it enters the ring it will enter in the position para to the amino group, if this position is not already filled or does not have the neighboring meta position filled with an unlike negative group. When the para position is filled, the bromine will go to the ortho position, if it is not already filled or does not have the neighboring meta position filled with an unlike negative group or the other ortho position filled with an unlike negative group. In the majority of cases, when one position, either meta or ortho, is filled with an unlike negative group, the bromine seems to take the position, whose corresponding position or whose neighboring position, is not filled by an unlike negative group. This substitution does not seem to vary in our work but seems to follow out the general law of isomerization, like the nitrogen halides of Chattaway and Orton.

The melting points and color, also the crystalline form, of some series, like the nitro-toluidines, are very regular, The 2-nitro-4-toluidine, when condensed with chloral, shows lemon-yellow needles, melting at 108-9° C, the 4-nitro-2-toluidine shows golden-yellow needles, melting at 142-3° C while the 3-nitro-4-toluidine

shows brownish-yellow needles and melts at 162-3° C. The regular rise in melting point and similiarity in crystalline form seem to fit the majority of cases where like compounds are studied in a series. It is not, however, a general law but will appear in the majority of cases.

## EXPERIMENTAL PART

### *DIVISION I*

#### THE ACTION OF BROMINE AND HCL UPON CERTAIN DI-PHENAMINE COMPOUNDS

#### (1) The action of Bromine upon Tri-chlor-ethylidene-di-phena-mine

*Action of two molecules of bromine*

The tri-chlor- ethylidene-di-phenamine, made according to A. Eibner's method[1] and purified by successive extractions with hot benzol, leaving behind an insoluble body of which we find no mention in Eibner's work, melting at 190-1°, was dissolved in the least amount of cold glacial acetic acid and bromine was added in the proportion of two molecules of bromine for each molecule of the condensation product. A white crystalline precipitate settled out, on cooling, showing large, scale-like crystals under the microscope and decomposing at 228-30°. It was easily soluble in alcohol, soluble in glacial acetic acid and amyl alcohol and insoluble in benzol, toluol, zylol, gasolene, carbon tetra-chloride and carbon disulphide.

An analysis by the Carius method gave the following result:

No. (1) 0.2000 gram of substance gave 0.2980 grams of AgBr.
No. (2) 0.2000 ,, ,, ,, ,, 0.2887 ,, ,, ,,

| Calculated for, | Found, |
|---|---|
| $C_6H_7NBr_2$, | No. (1) 63.40 p. c. |
| 63.24 p. c. of Br. | No. (2) 63.52 p. c. Br. |

This compound was then treated with sodium hydroxide to remove the hydrobromic acid and thus obtain the free amine, which was found to melt at 63°C. This free amine gave an acet-

[1]Ann. d. Chem. Ges. **302**: 340. 1890

derivative, on boiling with acetic anhydride, which melted at 160-3°. The formation of these two compounds from the free amine proved that it was para-brom aniline and that the original bromine derivative was para-brom aniline-hydro-bromide.

On examining the glacial acetic acid filtrate from the bromine reaction we were able to obtain oily drops of chloroform, when it was neutralized with sodium hydroxide and distilled with steam, showing that the chloral group had been split off by the action of bromine and proving all bromine to be in the ring or attached as the hydro-bromide. The other possibility is substitution in the $NH_2$ group.

*The action of one molecule of bromine*

When one molecule of tri-chlor-ethylidene-di-phenamine was treated with one molecule of bromine, in the same manner as in the previous experiment, the product had the same appearance but it decomposed at 282°. It was soluble in water or alcohol, insoluble in xylene, toluene, benzene, gasolene and carbon tetra-chloride. Glacial acetic acid was the most promising crystallizing medium for it was difficultly soluble in the cold solution but readily soluble in the hot.

An analysis of this compound by the Stepanoff method gave the following result:

No. (1) 0.2000 gram of substance gave 0.2167 grams of AgBr.
No. (2) 0.2000 ,, ,, ,, ,, 0.2155 ,, ,, ,,

| Calculated for, | Found, |
|---|---|
| $CH_2NBr$, | No. (1) 46.10 per cent. |
| 45.97 per cent Br. | No. (2) 45.85 ,, ,, |

The bromine derivative was then treated with a sodium hydroxide solution and the hydrobromic acid group taken off, giving back free aniline as the free amine. This was proved to be aniline by making the hydro-chloride and the acetate, each of which gave the proper melting point.

Chloroform was also detected in the glacial acetic acid filtrate from the bromination product.

From the foregoing experiments we would conclude:

*First*, that when tri-chlor-ethylidene-di-phenamine is treated

with bromine in a glacial acetic acid solution chloral is split off and a hydrobromide of aniline or the hydrobromide of a brominated aniline is formed, varying with the amount of bromine used in the bromination. And this would suggest that *Secondly*, when any amine condensation product is treated with bromine, the chloral residue will split off and the bromine will enter the ring or attach itself as a molecule of hydrobromic acid, according to the amount of bromine used and the nature of the condensation product.

POSSIBLE FORMATION OF NITROGEN BROMIDES

When the tri-chlor-ethylidene-di-phenamine is acted upon by bromine in glacial acetic acid solution or suspension, two compounds are formed which seem to be aniline hydrobromide and para brom aniline hydrobromide, but which show positive differences from them. They are, however, very unstable and change into aniline hydrobromide and para-brom aniline hydrobromide, on boiling with water, or tend to lose all halogens present and form aniline hydrobromide alone, when acted on by direct sunlight or on allowing the reaction product, obtained from the bromination of the tri-chlor-ethylidene-di-phenamine, to stand for twenty four hours in the original acetic acid solution, after bromination. It would be well to state, just at this point, that we have never been able to repeat all these results which follow, but many have been repeated, which would justify the assumption that a nitrogen bromide has been formed. The first bromine derivative that we shall take up will be the mono-brom derivative.

*The mono-brom derivative of Tri-chlor-ethylidene-di--phenamine*

In studying the action of one molecule of bromine on one molecule of tri-chlor-ethylidene-di-phenamine, we observed that, in one instance, our product was not aniline hydrobromide, as we formerly supposed, but differed from aniline hydrobromide, both in solubility and in melting point, so we undertook a careful study of its preparation and properties. The method of preparation which was used was the addition of one molecule of bromine, dissolved in glacial acetic acid in the ratio of one cubic centimeter of bromine to nine cubic centimeters of glacial acetic acid, to one

molecule of tri-chlor-ethylidene-di-phenamine, dissolved in the least amount of cold glacial acetic acid. After these two were mixed and the temperature kept below fifteen degrees, a white scaly precipitate settled out, melting at 282°; with a deep violet decomposition. The first point taken up was the solubility of this compound as compared to that of aniline hydrobromide. The unknown bromine derivative was found to be only partly soluble in water while the aniline hydrobromide was easily soluble. On boiling the unknown bromine derivative for one and one half hours, with water, a complete solution resulted from which pure aniline hydrobromide crystallized out. The unknown bromine derivative was not very easily soluble in concentrated hydrochloric acid, while the aniline hydrobromide was.

It was shown that the unknown bromine derivative formed aniline hydrobromide on boiling with water by making a solution of such a product alkaline with NaOH and obtaining the free amine, which was proved to be aniline, both by the calcium-hypochlorite and the iso-carbylamine tests.

Our next step was to compare the melting point of the unknown bromine derivative with that of aniline hydrobromide. We found that the unknown bromine derivative melted with a dark violet decomposition at 275-7°, but after boiling with water, it melted at 282°C and gave a brown colored liquid, showing no appreciable decomposition, which was exactly similiar to the original aniline hydrobromide.

The action of sunlight on the unknown bromine derivative and upon aniline hydrobromide showed a distinct difference, both in color and behaviour. The aniline hydrobromide did not change color during a day and a half exposure while the unknown bromine derivative showed a very marked change, turning dark brown and becoming a lumpy mass.

An analysis of this bromine derivative, made from the purest material we had, gave the following result:

No. (1) 0.2000 gram of substance gave 0.2184 grams of AgBr.
No. (2) 0.2000 ,, ,, ,, ,, 0.2167 ,, ,, ,,

| Calculated for | Found |
|---|---|
| $C_6H_5NBr$, | No. (1) 46.46 p. c. |
| 46.51 p. c. of Br. | No. (2) 46.10 p. c. |

This would also be a very good analysis for aniline hydrobromide since the two compounds differ only in the content of hydrogen and the aniline hydrobromide would give 45.97 per cent of bromine.

*Acids* have no apparent effect upon this compound except to form the corresponding salts, as the hydrochloride, hydrobromide and sulphate.

*Alkalies*, either hot or cold, gave the free amine, which was aniline, proving that all the bromine was in the side chain.

*Water* caused a change from the unknown bromine derivative to aniline hydrobromide, on boiling for one and one half hours.

We have not been able to get Chattaway and Orton's reactions for the nitrogen halides, which they claim to be general. Probably this was due to the fact that we are dealing with an unsubstituted nitrogen halide and they were dealing with a substituted one.

*Summary.*

We have shown that we have a body which has all its halogen in the side chain, not as the hydrobromide but as the halide, connected directly to the nitrogen, because, *First*, water does not dissolve our bromine derivative, while aniline hydrobromide is very soluble. *Second*, sunlight does not affect aniline hydrobromide while our compound is decomposed very rapidly. *Third*, on boiling with dilute alkaline solutions the halogen is removed, which would be impossible were the bromine in the benzene ring. *Fourth*, the melting point of aniline hydrobromide is clear and well defined while the unknown bromine derivative decomposes with a violet or purple decomposition at from five to seven degrees lower.

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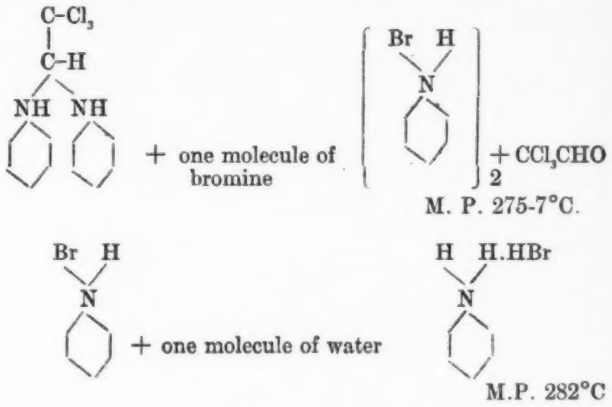
1 Journal London Chemical Society 75: 1046. 1899.

The reactions for this compound are represented thus:




*The di-brom derivative of Tri-chlor-ethylidene-di-phenamine*

The di-nitrogen bromide is formed when two molecules of bromine react with one molecule of tri-chlor-ethylidene-di-phenamine. This compound was obtained when the pure tri-chlor-ethylidene was suspended in glacial acetic acid and a 10 per cent glacial acetic acid solution of bromine added, little by little, care being taken to keep the temperature as low as fifteen degrees and the whole reacting mass well stirred. A fine white scaly precipitate was obtained, much more insoluble than the original condensation product, melting at 228-35°, with a violet or purple decomposition. This compound was thought to be para-brom aniline hydrobromide, both by its melting point and by its behaviour but a remarkable change was noticed in its preparation, which led us to suspect a di-nitrogen halide.

When one gram of the tri-chlor-ethylidene-di-phenamine was brominated, in the manner described above, and filtered off immediately, a compound melting at 228-235° with a purple decomposition was obtained, but if a similar preparation was allowed to stand for twenty-four hours, before filtering off the glacial acid, a compound was obtained, weighing less by one-third than the

former and showing a decomposition point at 282°. The action of this compound, which had been prepared in the former manner and melted at 228-235° was studied in connection with para-brom aniline hydrobromide and a comparison made of their several properties:

*Para-Brom-Aniline Hydrobromide*

Gave a melting point of 225°, with a violet decomposition. Dissolved easily in cold water. When boiled with water it did not change its M. P.

*Unknown Di-Bromide*

Gave a similar melting point and decomposition. Not so easily soluble in cold water. When boiled with water it changed its M. P. to 235°.

The action of sunlight on the two compounds showed that the unknown di-bromide was very unstable in the light. It changed rapidly in color with a simultaneous rise in melting point, while the para-brom aniline was unaffected. The unknown di-bromide changed its melting point from 228-35° to 247-55°, on allowing direct sunlight to act on it for four days, and it was completely changed to aniline hydrobromide on standing for three months in direct sunlight, giving a melting point of 280-2° and an analysis for one bromine atom in the molecule. This compound also gave free aniline on treating it with sodium hydroxide as proved by the iso-carbylamine test. The calcium-hypo-chlorite test also showed the presence of free aniline, thus giving direct proof that the compound was aniline hydrobromide.

The action of water on the para-brom-aniline hydrobromide and on our unknown bromine derivative was markedly different because with the para-brom aniline hydrobromide no change took place while with the unknown bromine derivative some para-brom aniline was formed which came out as an oil. This compound after standing some time will give some aniline hydrobromide and some para-brom aniline hydrobromide, on boiling with water, showing that originally all bromine was attached to the nitrogen and that it tends to break off on exposure to direct sunlight. On boiling this bromine derivative, which had been exposed to direct sunlight,

aniline hydrobromide is formed while in the case of the unexposed bromine derivative isomerization takes place and para-brom aniline hydrobromide is formed.

On analysis one sample of the di-bromide showed the following remarkable result:

0.2000 gram of di-bromide gave 0.2914 grams of AgBr.

| Calculated for | Found |
|---|---|
| $C_9H_5NBr_2$ | 62.00 per cent. |
| 63.74 per cent of bromine. | |

This analysis was made by boiling a sample of the di-bromide for fifteen minutes in a ten per cent sodium hydroxide solution, neutralizing with nitric acid and adding enough more to make the solution react strongly acid to litmus and then titrating the solution with $AgNO_3$, titrating the excess of $AgNO_3$ with $NH_4SCN$, according to Volhard's method. We were never able to repeat this work. Our results on different samples have ranged from 46.10 per cent of Br to 70.89 per cent of Br for the halogen content. It will be noticed that these figures run all the way from a mono-halogen derivative to a tri-halogen derivative, and that all are decomposed by a weak alkaline solution.

## SUMMARY

From the foregoing results we would conclude that we have a nitrogen halide, in which the nitrogen of the amine is joined to two bromine atoms, because:

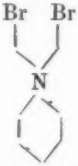
*First*, when our di-brom derivative, formed by the action of two molecules of bromine on one molecule of tri-chlor-ethylidene-diphenamine, was allowed to stand for twenty-four hours in the original brominated solution before filtering, we found a rise in melting point from 228-35° to 282°, and a compound formed which was proved to be aniline hydrobromide, both by its melting point and by the free amine which was aniline.

*Second*, when our unknown di-bromide is exposed to light for three months, it changes melting point from 228°-35° to 282° and a compound is formed which was proven to be aniline hydrobromide. This could not happen in the case of para-brom aniline hydrobromide.

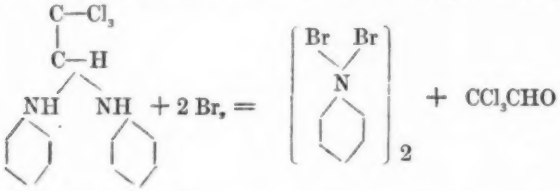
*Third*, On boiling with a dilute solution of an alkali, a per cent of bromine is obtained which would indicate that two bromine atoms were attached to the nitrogen for we find 62.00 per cent of bromine and the theory for two bromine atoms in the molecule would be 63.74 per cent of bromine. This would indicate that we have both of the bromine atoms attached to the nitrogen, because dilute alkalies will not take the bromine out of the benzene ring.

*Fourth*. Para-brom aniline hydrobromide can never change into aniline hydrobromide, by a simple exposure to sunlight, while our bromine derivative does. Para-brom aniline hydrobromide cannot give an analysis for two bromine atoms, on boiling with water or dilute alkali, while the unknown di-bromide does.

The formula for our di-bromide would then be:




and the reactions by which it is made would be represented thus:




(2) The Action of Bromine on Tri-chlor-ethylidene-di-para-nitro-Phenamine.

The object of this research was to establish the constitution of the compound obtained by brominating tri-chlor-ethylidene-di-para-nitro-phenamine, in a glacial acetic acid solution. This reaction was first carried out by A. S. Wheeler in this laboratory, in 1903 and the first general study of it was made by the author of this thesis, in the college year 1904-05. The study assumed some importance because all the condensation products of chloral with primary aromatic amines reacted smoothly with bromine in glacial acetic acid. At first we thought that we had the conden-

sation product with the hydrogen atom in the chloral residue substituted with bromine, although no decomposition product could be obtained which would prove this. Work several years later on the bromination of tri-chlor-ethylidene-di-phenamine threw a clear light on this compound and analogous ones. It was found not to contain any chlorine at all, by a displacement of all chlorine in the compound by bromine and weighing the precipitate as silver bromide. The chloral group is therefore split off in the bromination-as shown by making the filtrate from the reaction product alkaline and distilling, chloroform separating out in globules in the distillate. The bromine derivative is 2-6-di-brom-4-nitranilin with a melting point of 202-3°, that given for the above compound in Beilstein being 202.5°. The formula then is $C_6H_3N_2O_2Br_2$, with a theoretical percentage of bromine of 54.05 per cent. Our analysis by the Carius method showed the following result:

0.1000 gram of the bromine derivative gave 0.1286 grams AgBr.

| Calculated for | Found |
|---|---|
| $C_6H_3C_2N_2Br_2$ | 53.95 per cent of bromine. |
| 54.05 per cent of bromine. | |

These figures would also indicate a compound like our condensation product in which one hydrogen had been substituted for by one bromine atom, giving approximately the same theoretical per cent.

The solubility of this bromine derivative was found to be as follows: easily soluble in alcohol, hot or cold; difficultly soluble cold, easily soluble in hot glacial acetic acid; easily soluble in cold or hot acetone; insoluble in gasolene, xylene, toluene, or benzole.

*The Action of HCl*

When this bromine derivative was treated with concentrated hydrochloric acid no corresponding hydrochloride was formed because of the ease with which it was decomposed in any solution containing water, so we dissolved the 2-6-di-brom-4-nitranilin in cold acetone and passed in dry hydrochloric acid gas until a beautiful scaly, white precipitate came down, very similar in crystals line form to acet-anilide. This hydrochloride was easily decomposed by the addition of water, liberating hydrochloric acid and regenerating the original di-brom-nitranilin. An analysis of this

hydrochloride, by the Stepanoff method, showed the presence of one chlorine and two bromine atoms.

*The Action of HBr*

The hydrobromide of 2-6-di-brom-4-nitranilin was made by the addition of bromine to a hot solution of the di-brom nitranilin in glacial acetic acid. The acid derivative showed the same crystalline form and the same behavior towards water as the hydrochloride. It gave an analysis by the Stepanoff method which showed the correct percentage for three bromine atoms. This compound was very unstable, even in the air, for on exposing it to the air for a short time all the hydrobromic acid would be lost.

*Chlorination of Tri-chlor-ethylidene-di-para-nitro-phenamine*

On treating the tri-chlor-ethylidene-di-para-nitro-phenamine with chlorine, the 2,6-di-chlor-4-nitranilin was obtained, melting at 188°. It was a golden yellow compound crystalling out in long, prismatic needles.

(3) The action of bromine upon Tri-chlor-ethylidene-di-para-Tolamine

Para-toluidine and chloral were brought together in the proper proportions with benzene as a solvent.[1] The mixture was warmed slightly and the excess of benzene wrs driven off, allowing the tolamine to crystallize out. It became a thick paste in a very shor time and the mother-liquor, mechanically extracted, was dried out on an unglazed porcelain plate. The solid, obtained thus, was extracted several times with cold alcohol, by pouring alcohol over the product on a Buchner funnel and a pretty white, crystalline body was obtained. The melting point of this product was 115°, which identified it as A. Eibner's condensation product, described in the Annallen.

Ten grams of this condensation product were dissolved in the least amount of glacial acetic acid and two atoms of bromine were added very slowly, keeping the mass well stirred. The product obtained thus was filtered off and dried and found to represent an 85 per cent yield of para-toluidine hydrobromide. It was proved

[1]American Chemical Journal 22, 266. 1899.

to be para-toluidine hydrobromide by its decomposition point of 308-11°, its solubilities and its behaviour towards acids and alkalies. It was decomposed by water, made slightly alkaline with sodium hydroxide, giving free para-toluidine which melted at 48°. The free amine was also distilled and found to boil at 198-9°, which is the correct boiling point for para-toluidine.

Ten grams of the condensation product were then treated with four atoms of bromine in the manner just described. The result was a 95 per cent yield of the bromination product. This product was then treated with sodium hydroxide and shaken out with ether which gave ten grams of the free amine. On distilling this product, eight grams came over at 199-240°, five-tenths of a gram came over from 240-50° and the residue, left in the flask decomposed. The first fraction gave crystals on standing, which melted at 48°, showing that the majority of the product was para-toluidine. It was further identified by its hydrochloride and hydrobromide. The fraction above 240° gave needle like crystals, melting at 72-3° which must be 3,5-di-brom-4-toluidine. Another indication observed was its non-combining power with acids.

The mother-liquor after crystallization of the fraction 199-240°, and the fraction 240-50°, was an oil which would not crystallize, at room temperature, so the hydrobromide and the hydrochloride were made from this. The hydrochloride derivative decomposed at 212-22°, while the hydrobromide derivative gave a decomposition point at 252-5°, showing this oil to be 3-brom-4-toluidine, the bromine being ortho to the amino-group. The melting point of this compound should be 26° and it was found to be so.

This did not give us a preparation method for the brom-toluidine as it gave too much of a mixture.

(4) The Action of Bromine on Tri-chlor-ethylidene-di-ortho-Tolamine.

Ortho-toluidiné and chloral were brought together in the proper proportions to make the condensation product, according to the method of Wheeler and Jordan[1]. This was carried out by the addition of four parts of ortho-toluidine to three parts of chloral and then warming the mixture on a water bath for a short time.

The oil obtained in this manner was allowed to stand for a day to crystallize out. A hard solid mass was the result. We found that alcohol was really a better solvent than ether, which was used in the former method for recrystallizing the product. After two crystallizations from alcohol, the condensation product was found to be pure and gave a sharp melting point at 80°.

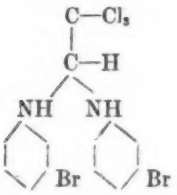
To this condensation product two atoms of bromine were added, or approximately one gram of the condensation product to 0.50 gram of bromine. This reaction was carried out in a glacial acetic acid solution and a very nearly 75 per cent yield was obtained. The resulting bromination product melted with a decomposition at 268°, but after recrystallization it came out in pearly, shining plates, melting with decomposition at 280°. This product was proven to be the 5-brom-2-toluidine-hydrobromide, both by its melting point and the melting point of its nitrate, which melted at 180-3°. The free amine melted at 58-60°.

This did not give a satisfactory method for the preparation of 5-brom-2-toluidine, as some ortho-toluidine was left unchanged and a little of the di-brom-toluidine was also formed, very similar to the action of bromine on the para-toluidine.

## *DIVISION II*

### THE CONDENSATION OF SOME PRIMARY AROMATIC AMINES WITH CHLORAL

Tri-chlor-ethylidene-di-meta-brom-phenamine




Molecular weight, *483*.

Melting point, 115-16°.

For this preparation twenty grams of meta brom-aniline were dissolved in 50 cc. of benzol and to this mixture were added nine grams of freshly distilled chloral. The reaction took place at once, with the liberation of a small amount of heat, giving a theoretical

yield of the crude product. This crude product was composed of two parts, a small by-product, which melted at 215-20° and the condensation product. These two compounds were separated by extracting the crude product with benzol thereby dissolving the condensation product and leaving the by-product undissolved. The benzole extract, which contained all the tri-chlor-ethylidene-di-meta-brom-phenamine in solution, was evaporated down over a steam bath to a sirupy constituency. Upon cooling and scratching the sirupy residue with a glass rod it yielded a substance melting at 98-101°, which crystallized from carbon tetrachloride in beautiful white needle-like crystals. After two recrystallizations from carbon tetra-chloride, the meltiag point was raised to 115-16°. The crystalline form of this compound, when seen under the microscope, appeared to be rhombic bi-pyramids, some crystals truncated on the apeces, others regular. and still others having one set of faces much larger than the other set.

*Water* had no effect on this condensation product, either when cold or when boiling hot. *Hydrochloric acid* gave the salt of the original meta-brom-aniline, while bromine gave the hydrobromide of the original meta-brom-aniline.

An analysis of this compound gave the following results, by the Carius method;

No. (1) 0.2000 gram of substance gave 0.1817 grams of AgCl and 0.1596 grams of AgBr.

No. (2) 0.2000 gram of substance gave 0.1802 grams of AgCl and 0.1581 grams of AgBr.

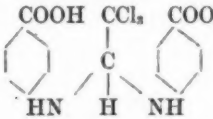
| Calculated for | | Found |
|---|---|---|
| $C_{14}H_{11}N_2Br_2Cl_3$ | (1) | 56.38 per cent, Total 22.43 per cent Cl. 33.95 per cent Br. |
| 56.24 per cent of Br. and Cl. | (2) | 55.89 per cent, Total 22.25 per cent Cl. 33.63 per cent Br. |

ACTION OF BROMINE

In making a careful study of the action of bromine on tri-chlor-ethylidene-di-meta-brom-phenamine, the method of Wheeler and Valentine was followed[1] for the separation of the several bromine derivatives. We hoped to obtain a method for the production of

3,4-di-brom-aniline which would give a better yield than the methods used at present. For this work 29.7 grams of the condensation product, which melted at 115-16°, were dissolved in the least possible amount of glacial acetic acid at room temperature. To this solution were added twenty grams of bromine also dissolved in glacial acetic acid, in the ration of one cubic centimeter of bromine to nine cubic centimeters of glacial acetic acid. A beautiful, scaly, white precipitate was obtained, which was filtered off and which weighed twenty grams. To the filtrate from this precipitate water was added and the tetra-brom aniline was precipitated. It weighed 2.6 grams. The bromine precipitate was treated with water and the tri-brom aniline was left undissolved while the di-brom aniline and brom-aniline hydrobromides were dissolved. This tri-brom aniline weighed 5.0 grams and the di-brom aniline weighed 8.0 grams, while only a trace of the original meta-brom aniline was obtained. We concluded from these results that this method possessed no advantage over the direct bromination of meta-brom aniline and so do not recommend it as a preparation method for 3, 4-di-brom aniline.

(2) Tri-chlor-ethylidene-di-para-amino-benzoic Acid




Molecular weight, *403.4*.

Melting point, 215-20°.

For a study of the action of para-amino-benzoic acid with chloral, we used two molecules of the acid, melting at 186-7°, to one molecule of chloral or about 10 grams of the acid to 5.5 grams of chloral. The aminobenzoic acid was suspended in 100 cc. of benzol and the chloral was added to this suspension after which the whole mass was warmed up on a water bath and then boiled for three hours under a reflux condenser. Most of the benzol was then evaporated off and the and the mixture was filtered while hot. This gave a compound which began to char at 186° and turned black at 220°, but which after recrystalling from glacial acetfc acid, melted at 215-220° with much decomposition. This was as pure as it was able to obtain the condensation product for further

recrystallizations did not raise the melting point. The crystalline form of this compound was not very well defined, the crystals occurring in colorless masses.

This compound was easily soluble in ethyl or methyl alcohol, difficultly soluble in glacial acetic acid and apparently insoluble in benzene, tolueme, xylene, carbon tetra-chloride and carbon di-sulphide.

The yield was 87.74 per cent of the theoretical or 13.6 grams of the condensation product from 10.0 grams of the para-amino-benzoic acid and 5.5 grams of chloral.

On analysis, this compound gave the following results by the Stepanoff method:

No. (1) 0.2000 gram of substance gave 0.05266 grams of chlorine.

No. (2) 0.2000 gram of substance gave 0.05517 grams of chlorine.

| Calculated for | Found |
|---|---|
| $C_{16}H_{13}O_4N_2Cl_3$ | (1) 26.33 per cent Cl. |
| 26.37 per cent Cl. | (2) 27.58 per cent Cl. |

THE ACTION OF BROMINE

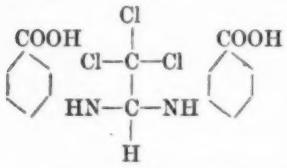
For a study of the action of bromine upon this condensation product we used 11.0 grams of the condensation product, 87 grams of bromine and mixed them together in 100 cc. of glacial acetic acid. Action was allowed to take place in the cold and the precipitate was filtered off. This precipitate was the hydrobromide of 3, 5-di-brom-para-aminobenzoic acid, as shown by its melting point, after treatment with water, which was 292-3° decomposing to a black mass. The action of water was to break off the hydrobromic acid and liberate the free amine. This free amine, when diazotized by the action of $NaNO_2$ and strong sulphuric acid in boiling alcohol solution, gave 3, 5-di-brom-benzoic acid, melting at 213-15°. This fully identified the bromine derivative.

When the condensation product is boiled with water no apparent change is noticed either in melting point or in general behavior.

When the condensation product is treated with concentrated

hydrochloric acid the corresponding para-aminobenzoic acid hydrochloride is formed, which when treated with sodium hydroxide and neutralized, gave the alkaline salt of para-amino-benzoic acid which could be acidified with acetic acid and precipitated with water, giving para-aminobenzoic acid.

Tri-chlor-ethylidene-di-meta-aminobenzoic Acid.



Molecular weight, *408.4*

Melting point, 240°.

For this preparation 10.0 grams of the meta-aminobenzoic acid were used, melting at 174°. This acid was dissolved in 100 cc. of benzol and to it were added 5.5 grams of freshly distilled chloral. This solution was boiled for one and one-half hours over a steam bath and a crude product of theoretical yield was obtained, after the excess of benzol had been evaporated off. The crude product was extracted for four or five successive times and the several extracts were mixed and allowed to crystallize out very slowly. This gave a white, crystalline mass which was soluble in benzol, acetone, amyl alcohol, glacial acetic acid and alcohol, insoluble in xylene, carbon-tetrachloride, ligroin, and cold or hot chloroform, and difficulty soluble in ether.

An analysis was made from 0.2000 gram of this sample which melted at 240° with a violet black decomposition and which had been crystallized from benzol and heated in an air bath for one and one-half hours to drive off the benzol. This analysis was carried out by the Stepanoff method and gave the following results for chlorine:

(1) 0.2000 gram of substance gave 0.2146 grams of AgCl.
(2) 0.2000 gram of substance gave 0.2104 grams of AgCl.

| Calculated for | Found |
|---|---|
| $C_{16}H_{13}O_4N_2Cl_3$ | (1) 26.50 per cent Cl. |
| 26.37 per cent Chlorine. | (2) 25.93 per cent Cl. |

The crystalline form of this compound resembled that of the

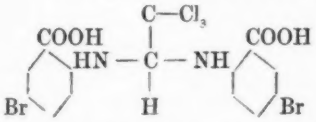
para-amino-benzoic acid condensation product in that it was composed of colorless crystal masses showing no definite form under the microscope.

THE ACTION OF BROMINE

The condensation product was then treated with bromine by dissolving 5.5 grams in 100cc. of glacial acetic acid and adding 4.3 grams of bromine, little by little. The yield from this was 7.0 grams of the bromine derivative, melting with a dark purple decomposition at 279-82°. This bromine body was boiled with water and a solution thus obtained. Free hydrobromic acid in the solution showed the product to be a salt. The aqueous solution on extraction with ether yielded a substance melting from 215-16°, which is the melting point of 5-brom-3-aminobenzoic acid. The proof was made more certain by the preparation of the sulphate and the hydrochloride.

When the condensation product is treated with concentrated hydrochloric acid, the acid salt of the free meta-aminobenzoic acid is formed, giving the free amine on boiling with a dilute alkaline solution and extracting with ether. This compound melts at 174°. Boiling water has no apparent effect on this condensation product.

Tri-chlor-ethylidene-di-5-brom-2-aminobenzoic Acid



Molecular weight, *561*.

Melting point, 174-5°.

For this preparation the 5-brom-2-aminobenzoic acid was made by brominating anthranilic acid in glacial acetic acid solution and decomposing the hydrobromide formed by boiling with water. It was purified by recrystallization from hot water according to the method of Wheeler and Oates.[1] Five grams of the 5-brom-2-aminobenzoic acid were dissolved in 100cc. of toluene and 1.8 grams of chloral were added. This solution was boiled for one and one half hours under a reflux condenser and then allowed to cool slowly. A white, crystalline precipitate, consisting of clusters of needle-like prisms settled out, melting at 174-5°. Analysis by the Stepanoff method gave the following results;

| Calculated for | Found |
|---|---|
| $C_{16}H_{11}O_4N_2Br_2Cl_3$ | (1) 28.01 per cent Br. |
| | 18.62 per cent Cl. |
| 28.52 per cent Br. 18.95 per cent Cl. | (2) 28.63 per cent Br. |
| | 18.96 per cent Cl. |

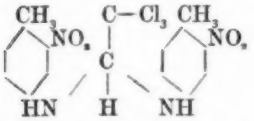
This compound was soluble in toluene, benzene, glacial acetic acid and alcohol. It was decomposed by water and all solvents containing water. When it is boiled with water it breaks down into chloral and 5-brom-2-aminobenzoic acid.

On treating this condensation product with concentrated hydrochloric acid, an effervescence is noticed, accompanied by the liberation of chloral and the reforming of 5-brom-2-aminobenzoic acid which melts at 216°. No hydrochloride of this compound is formed in aqueous solution, which is true of the original 5-brom-2-aminobenzoic acid.

ACTION OF BROMINE

When this product is brominated in a glacial acetic acid solution adding bromine until a permanent red color is obtained, a white, crystalline precipitate is formed, which melts at 234° decomposing to a black mass. On boiling this bromine derivative with water a solution is obtained, showing a blue fluorescence which is characteristic of 5-brom-2-aminobenzoic acid in water. On allowing this hot solution to crystallize out, yellowish-white needles are obtained which melt at 213-15°. A residue is always obtained which is insoluble in water, when the bromination product is boiled with water, melting at 221-3°. This is very probably one of the di-brom anthranilic acids.

Tri-chlor-ethylidene-di-ortho-nitro-para-Tolamine



Molecular weight, *433.35*.

Melting point, 108-9°.

For this preparation five grams of 2-nitro-4-toluidine were used, melting at 77.5°. This compound was dissolved in 100cc. of toluene and 2.6 grams of freshly distilled chloral were added, after

which the mixture was boiled for one and one-half hours. After boiling, the solution was cooled down and enough gasolene was added to precipitate out the compound, which had been formed in the reaction, giving an oil which solidified on standing on a moderately warm water bath for a half hour. This compound was soluble in alcohol, benzene, toluene, acetone and glacial acetic acid, being insoluble in gasolene and only slightly soluble in ether. After two crystallizations from a mixture of toluene and gasolene, a melting point of 108-9° was obtained, the substance melting down to a clear liquid.

An analysis of this compound was made by the Carius method and the following results were obtained:

No. (1) 0.1000 gram of substance gave 0.1003 grams of AgCl.
No. (2) 0.1000 gram of substance gave 0.1013 grams of AgCl.

| Calculated for | Found |
|---|---|
| $C_{16}H_{15}O_4N_4Cl_3$, | (1) 24.77 per cent Cl. |
| 24.52 per cent Chlorine. | (2) 25.02 per cent Cl. |

This compound gave on boiling with concentrated hydrochloric acid, a clear solution which on cooling gave long silvery-white needles, melting at 230-40° with a blackish decomposition. A sample of the pure 2-nitro-4-toluidine was converted into the hydrochloride by boiling with concentrated hydrochloric acid and it gave the same silvery-white needles melting at the same point with the same blackish decomposition. When the unknown hydrochloride was treated with ammonia and the free amine precipitated out it melted at 78-80°, showing that hydrochloric acid decomposed the condensation product, liberating chloral and forming the hydrochloride of 2-nitro-4-toluidine.

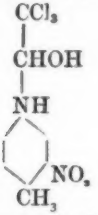
When this condensation product was boiled with water no change was produced in the melting point or crystalline form.

### ACTION OF BROMINE

0.20 gram of this condensation product was dissolved in the least amount of acetic acid, in the cold, and to this bromine was added also dissolved in glacial acetic acid. This gave a white, scaly, crystalline precipitate which melted at 240-50°, with a blackish decomposition. Some of the 2-nitro-4-toluidine was then taken and treated with hydrobromic acid, forming the hydrobro-

mide, which gave the same crystalline form and the same decomposition point at 240-50° thus proving the unknown bromine derivative to be the hydrobromide of 2-nitro-4-toluidine. The free amine, formed by neutralizing the hydrobromide with ammonia, gave a melting point of 75-80°, again proving the unknown bromine derivative to be the 2-nitro-4-toluidine hydrobromide. The bromine had liberated chloral and formed the bromide of the free amine with which the chloral had been condensed, no bromine entering the ring.

The Addition Product of 2-nitro-4-Toluidine and Chloral



Molecular weight, *299.35*.

Melting point, 187-8°.

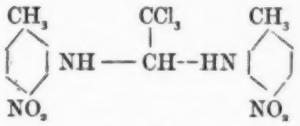
When the pure 2-nitro-4-toluidine was treated with chloral in the proportion of one molecule of 2-nitro-4-toluidine to one molecule of chloral, an addition product was obtained. For this preparation, 2.5 grams of the 2-nitro-4-toluidine were used. This was dissolved in benzol and two and one-half grams of chloral were added after which it was boiled for one hour over a steam bath, and then most of the benzol was evaporated off. On cooling the concentrated benzol solution, a fine crop of beautiful yellow needles separated out, melting at 147-8° but which after dissolving in benzol and precipitating out with gasolene, gave a melting point of 187-8° This compound was easily soluble in alcohol, benzene, glacial acetic acid and acetone, but it was insoluble in gasolene or xylene.

An analysis of this compound was made by the Carius method and gave the following results:

No. (1) 0.1000 gram of substance gave 0.1454 grams of AgCl.
No. (2) 0.1000 gram of substance gave 0.1457 grams of AgCl.

| Calculated for | Found |
|---|---|
| $C_9H_9O_3N_2Cl_3$ | (1) 35.91 per cent Cl. |
| 35.54 per cent Cl. | (2) 35.98 per cent Cl. |

Tri-chlor-ethylidene-di-para-nitro-ortho-Tolamine



Molecular Weight, *433.35*.
Melting point, 142°.

For this preparation 2.5 grams of 4-nitro-2-toluidine, melting at 109°, were dissolved in 50cc of benzol and then 1.5 grams of freshly distilled chloral were added. This solution was boiled for one and one-half hours over a steam bath, and a crude product of very nearly theoretical yield was obtained, after evaporating off the excess of benzol. This crude product was then dissolved in boiling benzol and filtered, giving an insoluble substance which melted at 215-30° with a blackish decomposition, and a filtrate which contained all the tri-chlor-ethylidene-di-para-nitro-ortho-tolamine. When this solution of the condensation product was evaporated down and the pure compound allowed to crystallize out, an 85 per cent yield was obtained which gave a melting point of 142-3°, melting down to a clear liquid. It was readily soluble in carbon tetra-chloride, benzol and glacial acetic acid but not so easily soluble in alcohol. Glacial acetic acid was found to be the best crystallizing medium, as it dissolved a large quantity while hot and on cooling a large amount of the compound crystallized out in long golden-yellow needles.

An analysis of this compound by the Carius method gave the following results:

0.2000 gram of substance gave 0.1961 grams of AgCl.

| Calculated for $C_{16}H_{15}O_4N_4Cl_3$, | Found |
|---|---|
| 24.52 per cent Chlorine. | 24.26 per cent Chlorine. |

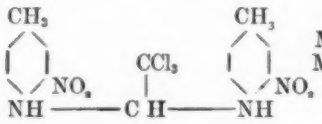
ACTION OF BROMINE

This condensation product, dissolved in cold glacial acetic acid, was treated with bromine also in glacial acetic acid solution (1-10), using 5.0 grams of the condensation product and enough bromine to produce a red color. A faint yellow, crystalline precipitate was obtained which melted, when recrystallized from glacial

acetic acid, at 215°, giving a blackish decomposition. When this bromine derivative was boiled with a 10 per cent solution of sodium hydroxide, it gave the free amine, which began to soften at 103° and melted down at 110°, proving that we had the hydrobromide of 4-nitro-2-toluidine formed and that when it was treated with sodium hydroxide the hydrobromic acid group was split off and the 4-nitro-2-toluidine was regenerated. No bromine entered the benzene nucleus.

When the condensation product was heated on a water bath with concentrated hydrochloric acid, it gave the corresponding hydrochloride. which when treated with ammonia, precipitated out the free amine, melting at 107-9°. This proved that the hydrochloride was the hydrochloride of 4-nitro-2-toluidine. The condensation product is stable in boiling water.

Tri-chlor-ethylidene-di-meta-nitro-para-Tolamine



Molecular Weight, *433.35*.
Melting point, 165-6°.

For this preparation 2.5 grams of the freshly prepared 3-nitro-4-toluidine, melting at 114-16°, were used. This compound was dissolved in 100cc. of toluene and to this solution were added 1.5 grams of freshly distilled chloral, after which the whole solution was heated for three hours over steam. A brownish-yellow mass of needles settling out on cooling which melted at 162-3°, but which after recrystallization from toluene, melted at 165-7°. This compound was easily soluble in toluene, benzene, gasolene, alcohol and glacial acetic acid.

An analysis by the Carius method showed the following result:
0.0644 grams of substance gave 0.0646 grams of AgCl.

| Calculated for | Found |
|---|---|
| $C_{16}H_{15}O_4N_4Cl_3$ | |
| 24.52 per cent Chlorine. | 24.77 per cent Chlorine. |

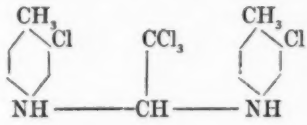
On treating this condensation product with concentrated hydrochloric acid and boiling, a dirty-white, crystalline precipitate

came out on allowing it to cool. This hydrochloride decomposed at 187-9°, with a black decomposition. On treating this hydrochloride with ammonia, the free amine was obtained in a very pure state, but which on recrystallization from alcohol gave a melting point of 114-16°, thus proving it to be the 3-nitro-4-toluidine hydrochloride. It will be noticed here that this hydrochloride is much more unstable than those formed from the other nitro toluidines, because it is a meta-nitro compound, which contains the nitro group in the most unstable position.

On boiling the condensation product with water it changed into a black, gummy mass and seemed to decompose to a large extent, for the melting point was lowered about twenty-five degrees.

On treating this condensation product with bromine, a brownish-white crystalline precipitate was formed, melting at 225-7°, with a blackish decomposition. When this bromine derivative is treated with sodium hydroxide, the free amine is liberated and precipitated out of solution, melting at 110-16°, thus proving it to be the hydrobromide of 3-nitro-4-toluidine.

Tri-chlor-ethylidene-di-meta-chlor-para-Tolamine



Molecular Weight, *412.25*.
Melting point, 110°.

The meta-chlor-para-toluidine, used in this preparation was made by chlorinating para-acettoluide according to the method of Wroblewski[1].

Five grams of the pure meta-chlor-para-toluidine, boiling at 218°, were dissolved in 100cc. of benzol and 3.5 grams of chloral were added. This solution was boiled for one hour and fifteen minutes and on cooling there separated out long. silvery-white needles melting at 181°. The filtrate from this was evaporated down to sirupy consistency over steam and allowed to crystallize out. This gave fine white needles, shorter than those of the other

[1]Ann. **168**: 196.

crop and melting at 110°. The first crop of crystals proved to be the addition product and will be taken up later in this paper, while the second crop of crystals proved to be the condensation product.

A sample of the second crop of crystals, melting at 110°, was dissolved in 95 per cent alcohol and filtered off from any of the addition product that might be present, since the addition product was not soluble in alcohol while cold. By this means a pure sample was obtained, melting sharply at 110°. An analysis by the Carius method gave the following result:

0.1000 gram of substance gave 0.1745 grams of AgCl.

| Calculated for | Found |
|---|---|
| $C_{16}H_{15}N_2Cl_5$ | |
| 42.96 per cent Chlorine. | 43.10 per cent Chlorine. |

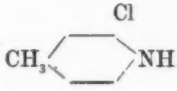
This compound was easily soluble in alcohol, benzol, toluene, xylene, ether and glacial acetic acid. It was much more soluble in alcohol than the addition product and by this means they were separated from each other.

When this condensation product was treated with concentrated hydrochloric acid and the solution heated over a steam bath until the excess of hydrochloric acid was driven off, a white, crystalline precipitate was obtained, melting to a black liquid at 230-35°, a majority of the substance in the melting point tube subliming. This compound was the hydrochloride of meta-chlor-para-toluidine, for when this compound was treated wirh ammonia and the hydrochloric acid group split off, an oil was obtained melting at from 20 to 23° and giving the same reactions as the original meta-chlor-para toluidine.

When the condensation product was dissolved in cold glacial acetic acid and treated with bromine, also in glacial acetic acid solution, (1-10), a white crystalline precipitate was obtained, crystallizing out in long colorless prisms. This bromine compound gave the melting point 78-80°. On treating this bromine derivative with ammonia, no change took place in the melting point, so it was concluded that the product was a bromine derivative of meta-chlor-para-toluidine which did not form a hydrobromide, but had substituted bromine in the ring. No compound which cor-

responded to this was found in the literature. It is probably the ortho-brom-meta-chlor-para-toluidine.

The addition product of chloral and meta-chlor-para-Toluidine



Molecular Weight, *288.8*
Melting point, 182°.

The first crop of crystals from the condensation of meta-chlor-para-toluidine, melting at 182°, was washed thoroughly with alcohol to remove all of the condensation product that might be present. Then a sharp melting point of 182-3° was obtained. A sample of this product was analyzed by the Stepanoff method and gave the following result:

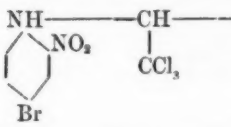
0.1000 gram of substance gave 0.2001 grams of AgCl.

| Calculated for $C_9H_9ONCl_4$ | Found |
|---|---|
| 49.10 per cent Cl. | 49.42 per cent Cl. |

This compound was only slightly soluble in alcohol, easily soluble in ether, benzol, gasolene, toluene, xylene and glacial acetic acid. It will be noted that it was much less soluble in cold alcohol than the condensation product and was purified by this method.

When this compound was treated with concentrated hydrochloric acid and bromine, the two reactions were similar to those for the condensation product, in that chloral was liberated in each case and the corresponding hydrochloride and the substituted bromine derivative were obtained.

Tri-chlor-ethylidene-di-para-brom-ortho-nitro-Phenamine



Molecular Weight, *563.35*.
Melting point, 190-1°.

The 4-brom-2-nitraniline, for this preparation, was made by treating para-brom acetanilide with a mixture of concentrated

sulphuric and nitric acids, according to the method of Hubner.[1]

Five grams of the pure 4-brom-2-nitraniline, melting at 110°, were dissolved in 100cc of toluene and about 6.5 grams of chloral were added, or about four times the amount of chloral required to make the condensation product. This solution was boiled for six hours, after which it was allowed to cool. Long, lemon-yellow needles separated out, melting at 232-3°, with a brownish-black decomposition. These crystals reacted with strong sodium hydroxide, forming a red compound, probably the hydroxy body, similar to the one made by Wheeler and Glenn.[2] This compound, melting at 232-3°, was very probably the addition product and was not investigated.

The filtrate from the lemon-yellow needles, which melted at 232-3°, was evaporated down to a sirupy consistency and a crop of smaller lemon-yellow crystals were obtained, melting at 190-1° and showing needle-like prisms under the microscope. This product was crystallized from toluene for two successive times but no change in melting point was obtained. This compound was soluble in benzene, toluene, xylene, alcohol and glacial acetic acid, fairly soluble in dilute alcohol, ether and carbon tetra-chloride.

An analysis of this compound showed the following result, when analyzed by the Carius method:

0.1000 gram of substance gave 0.1414 grams of AgBr and AgCl.

| Calculated for | Found |
|---|---|
| $C_{14}H_9O_4N_4Br_2Cl_3$ | 18.60 per cent Chlorine |

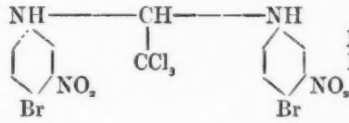
18.71 per cent Cl. 28.41 per cent Br. 28.13 per cent Bromine

On treating the condensation product with concentrated hydrochloric acid and evaporating off the excess of acid, an insoluble yellow powder was obtained, which melted at 108°. When this yellow powder was treated with ammonia, the melting point remained at 108-9°, showing that the hydrochloride formed had been decomposed by the moist air, or that no hydrochloride had been formed and that the condensation product had been split into chloral and 4-brom-2-nitranilin, which melts at 108-9°. Water had no apparent effect upon the condensation product. On treat-

[1]Ber. der deutsch Chem. Ges. 6: 766.
[2]Jour. Elisha Mitchell Scientific Society, 30, II, 63.

ing the condensation product with bromine, in a glacial acetic acid solution, a yellow crystalline compound settled out when the acetic acid solution was concentrated. This compound melted at 120-3° but rose in melting point to 130-1° when recrystallized from glacial acetic acid. This compound is very probably the 3, 4, 5-tri-brom aniline and a mixture of the lower bromine derivatives.

Tri-chlor-ethylidene-di-para-brom-meta-nitro-Phenamine




Molecular Weight, *563.35*.
Melting point, 147-9°.

For this preparation, five grams of the pure 4-brom-3-nitranilin which melted at 129-30°, were dissolved in 100cc. of benzol and to this were added 1.55 grams of chloral, after which the solution was heated over a water bath for two hours. This solution was allowed to cool and the by-product was filtered off. The filtrate was then evaporated down nearly to dryness or to a good sirupy consistency, and alcohol was then added, and the whole mass stirred well. Yellow needles came out in the cold solution, which were filtered off and dried. These crystals melted at 147-8° and on analysis by the Carius method gave the following result:

0.1000 gram of substance gave 0.0659 grams of AgBr. and 0.0746 grams of AgCl.

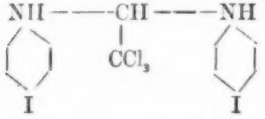
| Calculated for | Found |
|---|---|
| $C_{14}H_9O_4N_4Br_2Cl_3$ | 18.55 per cent Chlorine |
| 18.71 per cent Chlorine 28.41 per cent Br. | 28.01 per cent Br. |

When this condensation product was treated with concentrated hydrochloric acid and boiled, a light brown solution was obtained from which crystallized out long silvery white crystals, melting at 210-11° with a black decomposition. These crystals were not stable in the air or in a water solution, since they turned yellow and reformed the original 4-brom-3-nitraniline, similar to the reaction of the condensation product of the 4-brom-2-nitraniline. The free amine obtained by treating these crystals with water,

melted at 129-30°, showing this compound to be the hydrochloride of 4-brom-3-nitraniline.

When bromine was added to this condensation product, dissolved in the least amount of cold glacial acetic acid, a light yellow or whitish yellow crystalline compound settled out, appearing as fan shaped crystals under the microscope and melting at 88°. On boiling the product with sodium hydroxide, a reddish brown oil was obtained, which solidified on cooling and melted at 97°. This melting point was raised to 98-101° by boiling with hot water, which gave an oil that crystallized out on standing. This bromine derivative was the tri-brom-nitro-aniline (2.4, 6-tri-brom-nitraniline), proved by its melting point and its non-combining power with acids.

Tri-chlor-ethylidene-di-para-iodo-Phenamine




Molecular Weight, *567.35*.

Melting point, 123°.

The para-iodo-aniline, used for this preparation, was made by the action of iodine chloride upon acetanilide. The acet group was eliminated by boiling with concentrated hydrochloric acid. This gave long, silvery-white needles, melting at 63°.

For this preparation, 1.5 grams of the pure para-iodo-aniliue were used and to it was added 0.6 grams of freshly distilled chloral, after which 35cc. of benzol were added to the mixture and the whole solution was warmed up on a water bath for one hour. The by-product was then filtered off add the filtrate evaporated down to a sirupy consistency. Alcohol was then added to this sirupy mass and a steel gray mass of crystals were formed immediately. The crystal form of this compound was branching needles when seen under a microscope. This compound gave a melting point of 123°.

This iodo-condensation product was soluble in benzene, toluene, xylene, alcohol, acetone and glacial acetic acid, while it was not so soluble in dilute alcohol and gasolene.

An analysis of this compound by the Carius method gave the following results:

(1) 0.1000 gram of substance gave 0.1550 grams AgCl and AgI.

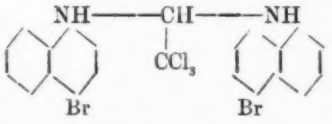
(2) 0.1000 gram of substance gave 0.0185 grams chlorine and 0.0471 grams of iodine.

| Calculated for $C_{14}H_{11}N_2Cl_3I_2$ | Found |
|---|---|
| | (1) 48.72 per cent I. |
| | 18.30 ,, ,, Cl. |
| 41.74 per cent I. and 18.70 per cent Cl. | (2) 41.71 ,, ,, I. |
| | 18.49 ,, ,, Cl. |

On treating this condensation product with concentrated hydrochloric acid, a hydrochloride is formed which decomposed at 206-10°, with the liberation of iodine, as proved by the purple vapor in the melting point tube. This hydrochloride yields, when treated with ammonia, para-iodo-aniline, melting at 63°. The hydrochloride of para-iodo-aniline also melted at 208-10°, with a purple colored vapor given off when it decomposed. These two reactions prove that the unknown hydrochloric acid derivative is the hydrochloride of para-iodo-aniline.

When this condensation product is treated with bromine, chloral is liberated and some para-iodo-aniline is regenerated as the hydrobromide, while still another part forms a brominated iodo-aniline. The iodo aniline was identified by its melting point of 63°, when the hydrobromide was treated with ammonia, while the unchanged portion, from the treatment with ammonia, melted at 83-9°, which was possibly a brominated iodo-aniline.

Tri chlor-ethylidene-di-4-brom-1-Napthylamine




Molecular Weight, *665*.

Melting point. 135-300°.

For this preparation, the 4-brom-1-napthylamine was prepared by treating acet napthylamine with bromine, forming the 4-brom-1-acet-napthylamine, and then removing the acet group by boiling for six hours with a saturated solution of caustic soda. This gave the 4-b.om-1-napthylamine which melted at 102°.

2.5 grams of this 4-brom-1-napthylamine were treated with enough chloral to dissolve it and this mixture was heated over a steam bath for two hours, stirring constantly. This mixture was then treated with 100cc. of toluene and boiled for a few minutes, after which it was allowed to cool. The addition of toluene was accompanied by a decided change in color and bulk. Gasolene was next added to this part solution and part suspension, precipitating out the remainder of the product in light purple flakes. This compound never melted but sublimed at 135-50°, leaving behind a black charred mass, which decomposed at 300° with an effervescence. This condensation product was soluble in toluene, xylene, alcohol and glacial acetic acid, but it was very insoluble in gasolene.

Three analyses, by the Carius method gave the following results:

No. (1) 0.1000 gram of substance gave 0.1176 grams AgCl and AgBr.

No. (2) 0.1000 gram of substance gave 0.1182 grams AgCl and AgBr.

No. (3) 0.1000 gram of substance gave 0.1189 grams AgCl and AgBr.

When these precipitates were treated with chlorine and all the bromine in them displaced by chlorine the resulting weights were less by 0.0126, 0.0128, and 0.0129 grams than the original precipitates. Now taking the greatest loss in weight. 0.0129, and calculating the amount of bromine we have:

0.0129 x 1.797 (factor to convert the loss in weight into bromine) equals 0.0232 grams of bromine.

0.0232 divided by 0.4255 will give the amount of silver bromide which is 0.0545 grams of AgBr.

0.1189 (weight of the original precipitate) minus 0.0545 will give the amount of AgCl present in the original precipitate which is 0.0644 grams of AgCl.

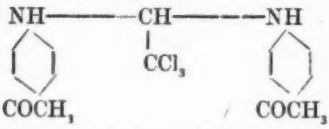
0.0644 grams of AgCl equals to 0.0159 grams of chlorine.

| Calculated for $C_{22}H_{13}N_2Cl_3Br_2$ | Found |
|---|---|
| 15.99 per cent chlorine | 15.90 per cent chlorine. |
| 24.06 per cent bromine. | 23.20 per cent bromine. |

The reason that we have assumed that this compound has such a formula, that is with one molecule of toluene of crystallization, is because of the fact that three analyses from three samples made at three different times show such a constant value for the halogen content, and such a constant value for the loss is weight when the bromine is replaced by chlorine. These values do not indicate an addition product nor a condensation product without toluene of crystallization because the percentages of these two products are very much larger than that obtained from our product, as to the halogen content. We find however that when this compound is treated with hydrochloric acid, the original 4-Br-1-napthylamine is regenerated and chloral is liberated. The first of these compounds is detected by its melting point and by its behavior, while chloral is obtained by distilling a mixture of this condensation product and hydrochloric acid, after it has been made strongly alkaline with sodium hykroxide. Chloroform can be detected by a faint odor and by the iso-carbylamine odor, with aniline and sodium hydroxide, thus proving the presence of the chloral group. Now since this compound cannot be the simple condensation or the simple addition product, which are the only two simple chloral compounds, and since it does contain chloral it undoubtedly contains toluene of crystallization. When the reaction product of chloral and 4-brom-1-napthylamine is treated with toluene a perceptible change takes place and the compound becomes more bulky, so this led us to the belief that one or more molecules of toluene were held mechanically as toluene of crystallization. When these several values were calculated, for one, two and three molecules of toluene, it was found that one molecule approximated our result the closest. In order to prove this it was attempted to heat an air dried sample to constant weight at 150°, but this failed for the compound sublimed and gave a white crystalline compound exactly similar to the original 4-brom-1-napthylamine when it was heated. From this we saw that we had a dissociation of the condensation product into chloral and the original 4-brom-1-napthylamine, which would take place as low as 100°. It was possible to get a loss in weight which was equal to 7.83 per cent of the total weight at 80°, but here also the decomposition stopped the

work for it began to decompose as low as 80° on prolonged heating. The theoretical for loss in weight for one molecule of toluene is 13.84 per cent.

Tri-chlor-ethylidene-di-para-Aminoacetophenone




Molecular Weight, *399.35*.

Melting point, 162°.

For this preparation 2.0 grams of the para-aminoacetophenone melting at 106-8°, were used and to it was added one gram of chloral. After this mixture had been triturated well in a beaker with a stirring rod, 50c. c. of toluene were added and the whole solution boiled which caused a flocculent whitish-yellow precipitate to settle out. This bye-product was filtered off and the filtrate concentrated to about half of its bulk over steam. On cooling large colorless crystals came out, showing thin rectangular plates under the microscope, when recrystallized out from dilute alcohol. Some of these rectangular plates showed a very uniform rounding off of the corners, presenting an elliptic form. This compound melted at 162° to a red liquid and gave on analysis, by the Carius method, the following result;—

0.0700 gram of substance gave 0.0747 grams AgCl.

| Calculated for, | Found |
|---|---|
| $C_{18}H_{17}O_2N_2Cl_3$, | |
| 26.63 per cent chlorine. | 26.36 per cent chlorine. |

This compound was soluble in toluene, benzene, xylene, and alcohol. It was also soluble in hot, dilute alcohol, but very insoluble when cooled down, so this gave a very good crystallizing medium for purification.

When this condensation product was treated with concentrated hydrochloric acid and warmed on a water bath, a yellowish-white, crystalline compound settled out, melting at 180-1°, giving a red colored decomposition. The action of hydrochloric acid upon the free aminoacetophenone gave a compound melting at the same place and giving the same red colored decomposition, show-

ing the unknown hydrochloride to be the hydrochloride of para-aminoacetophenone.

The action of bromine upon this condensation product was somewhat complicated, for we were not able to get back all the original free amine as the hydrobromide. When a cold saturated solution was treated with one molecule of bromine and allowed to cool, a light, greenish-yellow crystal mass came out, melting at 180°, to a red liquid and giving a slight decomposition. This bromine derivative, on treating with strong ammonia, gave an oil and a red colored solid. The red colored solid was very probably an hydroxy derivative of the bromine compound, which decomposed with water, while the oil solidified and gave a melting point of 108-10° when it was allowed to cool and crystallize out. This latter was very probably the original aminoacetophenone, but the red colored liquid and the red colored oil could not have been, since the aminoacetophenone gave no red color when boiled with an alkali. The melting point of the red colored compound was not determined for it decomposed into an oil so fast that it was nearly impossible to get a pure sample with which to work.

The action of Chloral upon Tri-chlor Aniline.

Alexander Einner, in the Annallen,[1] says that it is impossible to condense with chloral an amine, in the benzene ring of which there are three or more negative groups. Having been able to condense some amines which had two unlike negative groups in the benzene ring, it was thought that by the use of a higher boiling point solvent it might be possible to get a condensation to take place and if not by the higher boiling point solvent, why the high pressure of the sealed tube might cause the tri-chlor aniline and chloral to condense. The results of this work were not satisfactory, since it was impossible to get the condensation reaction to take place between the tri-chlor aniline and chloral. The results of this work are given below:

(1). 1.0 gram of tri-chlor aniline was used and to it was added one gram of chloral. This mixture was dissolved in xylene

[1]Annallen, **302**: 340-330.

and boiled for six hours. At the end of this time the tri-chlor aniline crystallized out as if no chloral had been present, melting at 77-8°. No change had taken place.

(2). 1.0 gram of the tri-chlor aniline was used and to it was added 1.0 gram of chloral. This mixture was dissolved in toluene and boiled for six hours. At each two hour interval a small amount of substance was taken out and allowed to crystallize, by evaporating down over steam. No change had taken place for the three samples each melted at 77-8°, showing that it was the unchanged tri-chlor aniline.

(3). Tri-chlor aniline and an excess of chloral, without a solvent, were heated up in a sealed tube and temperature kept at 100° for four hours. Two samples were taken out, one at the expiration of two hours and the other at the expiration of four hours.

Neither sample showed a change, for each melted at 77-8° and showed the long, silvery-white needles of tri-chlor aniline.